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Polychlorinated biphenyls and organochlorine pesticides in plastics ingested by seabirds

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ABSTRACT

The occurrence of plastic objects in the digestive tract was assessed in eight species of Procellariiformes collected in southern Brazil and the occurrence of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the ingested plastics pellets and plastic fragments was evaluated. PCBs were detected in plastic pellets (491 ng g^{-1}) and plastic fragments (243–418 ng g^{-1}). Among the OCPs, *p,p′*-DDE had the highest concentrations, ranging from 68.0 to 99.0 ng g^{-1}. The occurrence of organic pollutants in post-consumer plastics supports the fact that plastics are an important source carrying persistent organic pollutants in the marine environment. Although transfer through the food chain may be the main source of exposure to POPs to seabirds, plastics could be an additional source for the organisms which ingest them, like Procellariiformes which are the seabirds most affected by plastic pollution.

Plastics are synthetic organic polymers that can be found in coastal and oceanic waters worldwide. These products are among the most persistent macroscopic pollutants in the marine environment (Rios et al., 2007) and can be harmful to biota. A number of studies have reported the ingestion of plastics by fish, sea turtles and seabirds (Furness, 1985; Colabuono et al., 2009; Tourinho et al., 2010) as well as their harmful effects on organisms (Ryan and Jackson, 1987; Ryan, 1988; Pierce et al., 2004).

Plastic debris has been found to accumulate contaminants due to its hydrophobic nature (Mato et al., 2001; Rios et al., 2007). There have been several reports of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), such as DDTs, in plastic pellets collected from beaches around the world (Mato et al., 2001; Endo et al., 2005; Ogata et al., 2009). Rios et al. (2007) have reported the occurrence of organic contaminants in post-consumer plastic debris and state that these plastics are important sources of persistent organic pollutants (POPs).

PCBs and OCPs are organic contaminants of great concern, recognized as POPs, due to their hydrophobic nature and persistence in the environment, which allows these compounds to be bioconcentrated and biomagnified throughout the food chain (Ritter et al., 1995; Lallas, 2001). There is concern regarding the possible transfer of these contaminants from plastics to marine organisms that ingest them. This may be a significant pathway for the chemicals in plastics to enter marine organisms (Ryan et al., 1988; Derraik, 2002; Tanabe et al., 2004).

Seabirds, especially Procellariiformes (albatrosses and petrels), are a group of marine animals most affected by plastic pollution. These birds often confuse plastics with prey and these objects can remain in their digestive tract for several months before being eliminated (Ryan and Jackson, 1987). Therefore, the Procellariiformes have the highest incidence of plastic ingestion among seabirds (Furness, 1985; Azzarello and Van Vleet, 1987; Ryan, 1988; Tourinho et al., 2010). Thus, in addition to transfer through the food chain, plastic ingestion may be another source of organic contaminants for these top predators.

In the present study, the occurrence of plastic objects in the digestive tract was assessed in eight species of Procellariiformes collected in southern Brazil and the occurrence of PCBs and OCPs in the ingested plastics was evaluated.

Thirty-four White-chinned petrels (*Procellaria aequinoctialis*), three Spectacled petrels (*Procellaria conspicillata*), six Great shearwaters (*Puffinus gravis*), six Manx shearwaters (*Puffinus puffinus*), 31 Black-browed albatrosses (*Thalassarche melanophris*), 13 Atlantic Yellow-nosed albatrosses (*Thalassarche chlororhynchos*), three Wandering albatrosses (*Diomedea exulans*) and one Tristan albatross (*Diomedea dabbenena*) were collected on the beaches in the state of Rio Grande do Sul (Brazil) as well as from longline fisheries off southern Brazil (29°S–34°S; 45°W–52°W) between 1991 and 2008 (Fig. 1).

All plastics found in the proventriculus and ventriculus of the birds were collected, dried at room temperature and separated into three categories: plastic pellets, which have either polyethylene or polypropylene as the raw material in the form of small spheres or cylinders and that are melted and molded to create plastic products (US EPA, 1992); plastic fragments, which are rigid pieces of

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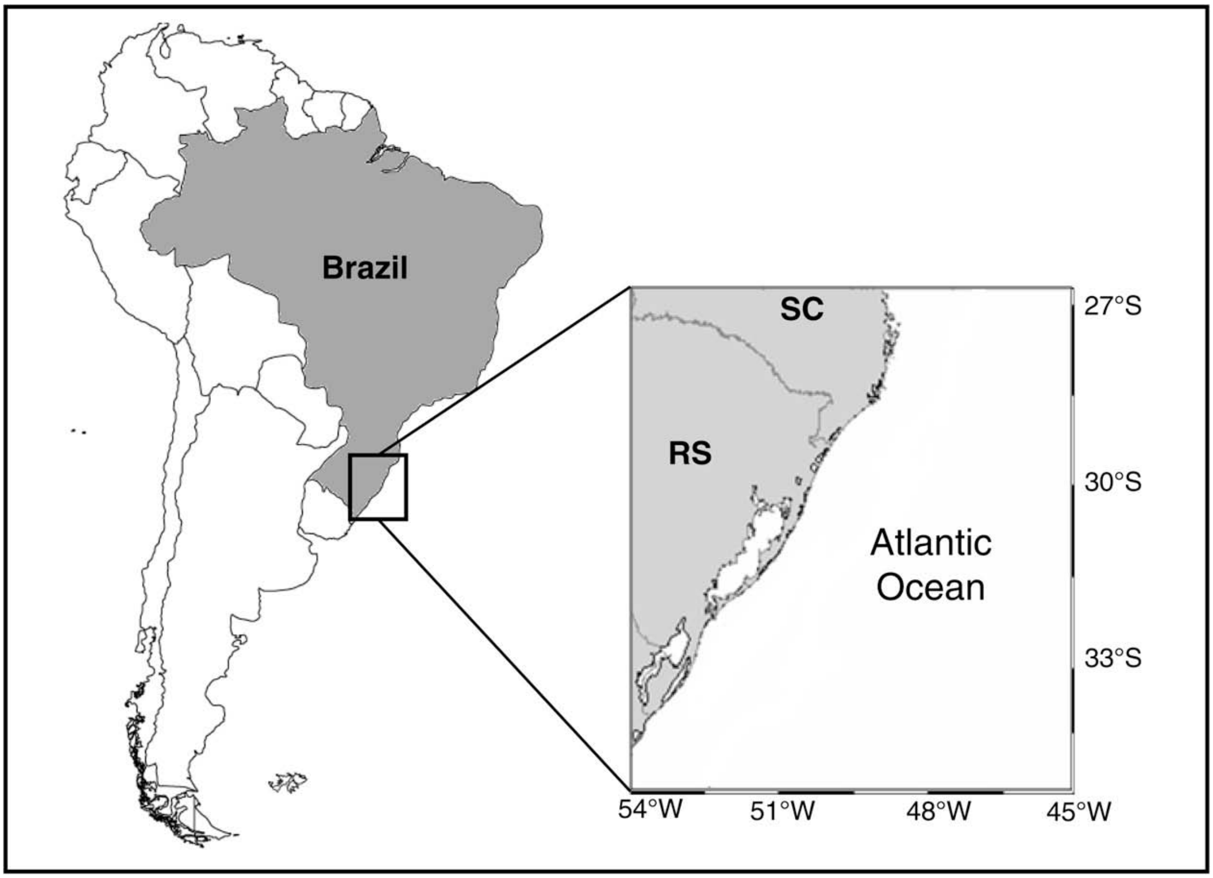

Fig. 1. Location of the study area; birds were collected along the coast of the state of Rio Grande do Sul (RS) and from longline fisheries off southern Brazil.

larger objects or pieces of plastic bags and packaging either discarded or lost at sea; and nylon line. The samples were wrapped in aluminum foil and frozen at −20 °C until analysis.

Plastic pellets and plastic fragments were pooled and analyzed for the presence of PCBs and OCPs. The plastics were not sorted by size, shape or color. Analytical procedures followed those described by the UNEP (1992), with some adaptations. Briefly, the plastics (0.6 g for industrial plastic pellets; 1.0 g for plastic fragments) were extracted in a Soxhlet apparatus for 8 h using 80 ml of *n*-hexane and methylene chloride (1:1, v/v). Prior to extraction, 2,2′,4,5′,6-pentachlorobiphenyl (PCB 103) and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl (PCB 198) were added to all samples, blanks and reference material as surrogates for chlorinated pesticides and PCBs. Extracts were cleaned using a chromatographic column with 3.2 g of alumina (5% water deactivated), eluted with 20 ml of *n*-hexane and methylene chloride (7:3, v/v). The extract was concentrated to a volume of 1.0 ml in hexane. The internal standard 2,4,5,6-tetrachlorometaxylene (TCMX) was added before gas chromatographic analysis. A procedural blank was run with the set of samples.

The identification and quantification of chlorinated pesticides was performed with a Agilent Technologies 6890N gas chromatograph with an electron capture detector (GC–ECD) using a 30 m × 0.25 mm i.d. capillary column coated with 5% phenyl-substituted dimethylpolysiloxane phase (0.25 μm film thickness). Automatic splitless injections of 2 μl were applied and the total purge rate was adjusted to 50 ml min^{-1}. Hydrogen was used as the carrier gas (constant pressure of 40 kPa at 100 °C), while nitrogen was the make up gas at a rate of 60 ml min^{-1}. Injector and detector temperatures were 280 and 320 °C, respectively. Oven temperature was programmed as follows: 70 °C for 1 min, raised at 40 °C min^{-1} to 170 °C, then raised at 1.5 °C min^{-1} to 230 °C (held for 1 min) and at 30 °C min^{-1} to 300 °C with a final hold of 5 min.

PCBs were quantitatively analyzed using an Agilent Technologies 5973N gas chromatograph coupled to a mass spectrometer (GC–MS) in selected ion mode (SIM 70 eV), using a 30 m × 0.25 mm i.d. capillary column coated with 5% phenyl-substituted dimethylpolysiloxane phase (0.25 μm film thickness). The volume injected was 1 μl in automatic splitless mode. Helium was used as the carrier gas (constant flow of 1.1 ml min^{-1}). The interface, source and quadrupole temperatures were 280, 300 and 200 °C, respectively. Oven temperature was programmed as follows: 75 °C for 3 min, raised at 15 °C min^{-1} to 150 °C, then raised at 2.0 °C min^{-1} to 260 °C and at 20 °C min^{-1} to 300 °C, with a final hold of 1 min.

For quality assurance/quality control (QA/QC), the analytical methodology was validated using a standard reference material (SRM 1941b – organics in marine sediment) purchased from the National Institute of Standards and Technology (USA). SRM 1941b was analyzed in duplicate and average recovery of analytes was 95%. The recovery of analytes in spiked blanks and matrices produced satisfactory results (80–120%). Analytes in procedural blanks were subtracted from the samples. Method quantification limits (QL) ranged from <0.08 to 6.27 ng g^{-1}. Laboratory check solutions were routinely injected into GC–ECD and GC–MS to confirm instrument accuracy and precision. Calibration of the instruments was performed using a nine-level analytical curve. Quantification of analytes followed the internal standard procedure. Surrogate recoveries were acceptable (mean: 93.33; standard deviation: 3.61).

The chlorinated pesticides analyzed in the present study were DDTs (*o,p*′-DDT, *p,p*′-DDT, *o,p*′-DDD, *p,p*′-DDD, *o,p*′-DDE and *p,p*′-

DDE), HCHs (α, β-, δ- and γ-isomer), chlordanes (α-, γ-chlordane, oxychlordane), cyclodienes (aldrin, isodrin, dieldrin, endrin, heptachlor, heptachlor epoxide A and B, endosulfan I and II), metoxychlor, HCB and mirex. A suite of 51 PCBs was also investigated, including the following IUPAC numbers: 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 77, 81, 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 169, 170, 174, 177, 180, 183, 187, 189, 194, 195, 199, 203, 206 and 209.

After the chemical analyses, some physical properties of the plastics, such as buoyancy in sea water (density = 1.02 kg/m^3), color, weight and size were also recorded.

Plastic objects were found in 28% of the birds, with the following frequencies of occurrence (FO) by species: 44% in White-chinned petrels; 33% in Spectacled petrels; 100% in Great shearwaters; 17% in Manx shearwaters; 6% in Black-browed albatrosses and 8% in Atlantic Yellow-nosed albatrosses. No plastic was found in the digestive tract of Wandering and Tristan albatrosses. Petrels usually have higher occurrence of ingestion of plastics than albatrosses (Colabuono et al., 2009; Furness, 1985), as demonstrated in the present study, perhaps because they can accumulate solid objects in the digestive tract for a long time (Ryan and Jackson, 1987).

Plastics found in the digestive tract of the birds studied consisted of small plastic fragments (1.7–51.5 mm; 0.001–0.195 g), plastic pellets (3.2–5.3 mm; 0.0176–0.0268 g) and nylon lines (16.5–186 mm; 0.1078–0.0019 g). In the pooled sample, plastic fragments predominated in number (63%) and FO (17%). Nylon lines accounted for 17% of the objects (FO of 10%) and plastic pellets accounted for 16% of objects (FO of 6%). Plastic fragments also predominated in previous studies (Ryan, 2008; Colabuono et al., 2009; Tourinho et al., 2010). Ryan (2008) has reported a decrease of the ingestion of plastic pellets by seabirds in more recent years. In the present study, pellets were found only in great shearwaters. Moreover, nylon lines predominated in number in Black-browed and Atlantic Yellow-nosed albatrosses and no fragments or pellets were found in the digestive tract of these species (Fig. 2). Nylon lines may be linked with fisheries and their presence in the stomach contents of these birds reaffirms the strong interaction of these albatrosses with fishing vessels.

PCBs and OCPs were detected in both plastic pellets and plastic fragments. Table 1 displays concentrations of OCPs and total PCBs found in fragments and pellets ingested by the seabirds studied. The congener profiles of the PCBs found in the plastic pellets and plastic fragments were rich in higher chlorinated congeners, such as PCB 118 (pentachlorobiphenyl), PCBs 138 and 153 (hexachlorobiphenyls) and PCBs 170 and 180 (heptachlorobiphenyls). The PCB homolog distribution is displayed in Fig. 3. Mato et al. (2001) found that the congener profiles of PCBs in plastic pellets and in the particulate phase of sea water were enriched in higher chlorinated congeners (132, 153 and 138), which supports the hypothesis of a preferential partition of hydrophobic compounds (higher chlorinated congeners) on non-polar plastic surfaces. Rios et al. (2007) also found a predominance of penta and hexachlorobiphenyls in post-consumer plastics at coastal sites in Hawaii and California.

Among the OCPs, *p,p′*-DDE had the highest concentrations, ranging from 68.0 to 99.0 ng g^{-1} (Fig. 4). These concentrations are two orders of magnitude lower than the highest concentration reported by Rios et al. (2007) in plastics collected at an industrial site in the USA. After discharge in aquatic environments, *p,p′*-DDT breaks down (under anaerobic condition or by biotransformation) into *p,p′*-DDE (Kale et al., 1999), which is one of the most commonly found OCPs in the tissue of marine animals. In a recent study, Ogata et al. (2009) reported the occurrence of DDTs (DDT, DDD and DDE) in plastic pellets collected along coastal areas of North America, Europe, Asia, Africa and Oceania. On the west coast of the USA and the coast of Vietnam, sites where substantial amounts of DDT-pesticides were used in the past for agricultural production or anti-mosquito operations, the concentrations of total DDTs are twofold to fourfold higher than the concentrations found in the pellets studied here. However, unlike what occurred in the present study and what has been reported by Rios et al. (2007), DDT was more, or as abundant as its metabolites DDD and DDE.

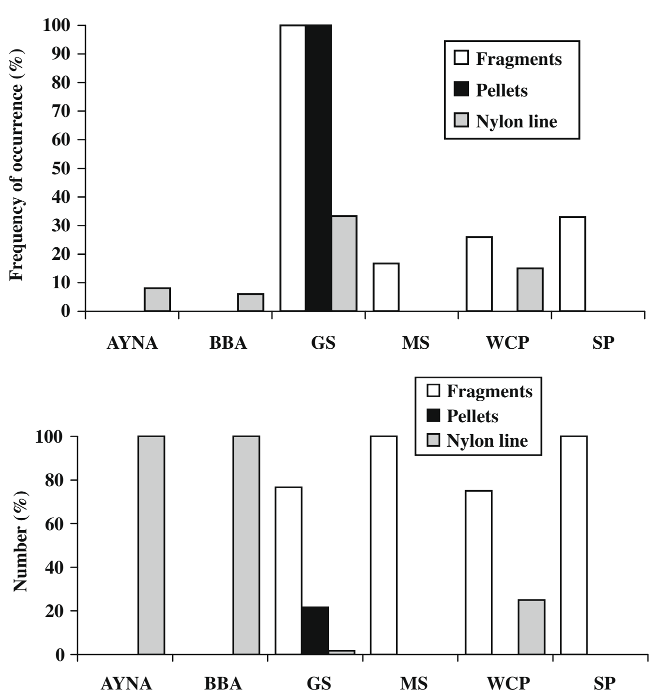

Fig. 2. Relative frequency of occurrence and number of plastics found in the digestive tract of Atlantic Yellow-nosed albatross (AYNA), Black-browed albatross (BBA), Great shearwater (GS), Manx shearwater (MS), White-chinned petrel (WCP) and Spectacled petrel (SP).

Table 1
Concentrations (ng g^{-1}) of organochlorine pesticides and total PCBs found in plastics ingested by Procellariiformes.

Compound	Plastic pellets	Plastic fragments
PCBs	491	243–418
HCB	12.4	15.1–17.5
Chlordanes	5.22	4.29–14.1
Cyclodienes	2.58	2.41–50.9
DDTs	68.0	64.4–87.7
Mirex	6.48	7.36–14.6

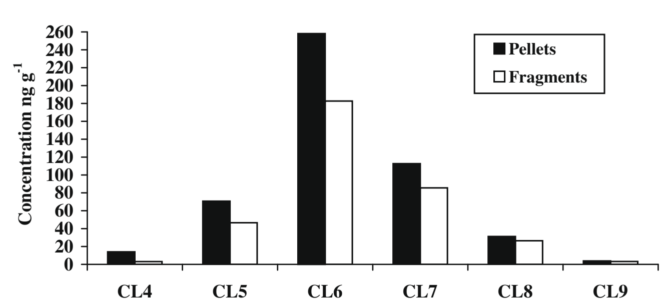

Fig. 3. PCB homolog distribution in plastics found in the digestive tract of Procellariiformes.

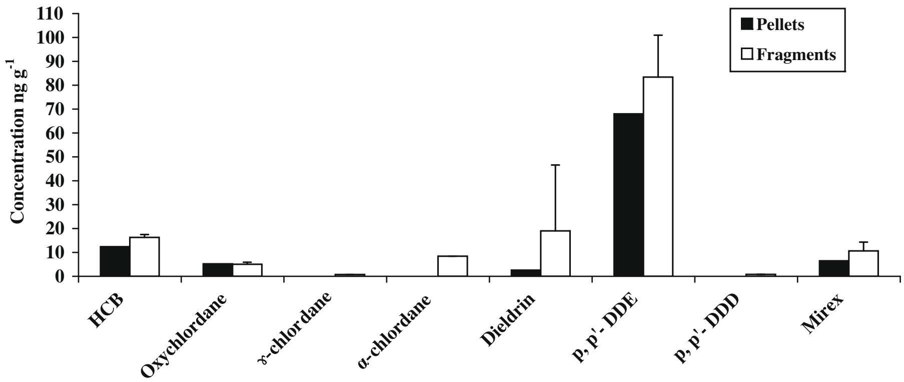

Fig. 4. Concentrations of chlorinated pesticides in plastics found in the digestive tract of Procellariiformes.

Other OCPs, such HCB, chlordane, dieldrin and mirex, also occurred in pellets and fragments, but at lower concentrations (Fig. 4). These pesticides are also usually found in marine environments due to their high persistence (e.g., oxychlordane, mirex, dieldrin) and considerable dispersion capacity (e.g., HCB) (Calamari et al., 1991).

The variation in contaminant concentration in plastics is associated with many factors. One such factor is the residence time of plastics in the environment. Endo et al. (2005) reported that older plastic pellets that were fouled and discolored (yellowed) contained greater amounts of PCBs than white pellets (non-fouled and non-discolored) that probably spend less time in the environment. Although the samples were grouped in the present study, most of plastic fragments (59%) and pellets (69%) were white and non-fouled and total PCBs concentrations were as high as those described by Endo et al. (2005) for fouled and yellowed pellets. Another factor is the mobility of the plastics (Endo et al., 2005). If plastics can float on the ocean surface, they can be carried to different places and the pollutant content in the plastics will reflect the pollution along the entire transport path following discharge (Mato et al., 2001). All plastics ingested by the birds in the present study, with the exception of one nylon line piece (0.61%), were less dense than sea water and were therefore able to float on the ocean surface. Consequently, these plastics could float long distances and take on contaminants from sea water before being ingested by the birds.

Organochlorine contaminants have been found in the tissues of majority of seabirds around the world, including Procellariiformes (Ryan et al., 1988; Guruge et al., 2001a,b). The profiles of organochlorine compounds found in the plastics analyzed in the present study are similar to those seen in these seabirds: i.e., a predominance of higher polychlorinated biphenyls and *p,p′*-DDE (Guruge et al., 2001a,b; Ryan et al., 1988). The predominance of some compounds in seabirds is associated with factors such as metabolism, tissue affinity and contamination source (Matthews and Dedrick, 1984). Although transfer through the food chain may be the main source of exposure of POPs to seabirds (Borgå et al., 2004), plastics could be an additional source for seabirds, which often ingest these objects.

Persistent organic pollutants have been found in tissues of seabirds as well as several types of plastics. The fact that plastics have a great potential as one of the sources of these compounds for marine animals that ingest them has been cited by several authors (e.g., Ryan et al., 1988; Mato et al., 2001; Endo et al., 2005; Rios et al., 2007). Considering this, further studies on POPs contamination in seabirds with high frequencies of plastic ingestion, such as Procellariiformes, and the development of research that links such information are essential to understanding whether (and how) the transfer of organic pollutants from plastics to marine organisms occurs.

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